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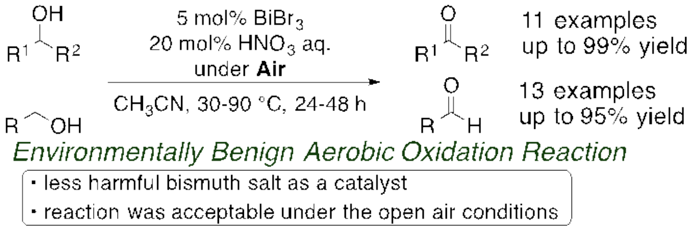

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# Aerobic Oxidation of Alcohols Using Bismuth bromide as a Catalyst

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ABSTRACT

We developed an environmentally friendly method for aerobic oxidation of alcohols using a commercially available, relatively benign bismuth salt as a catalyst. We found that the catalytic combination of $BiBr_3$ with nitric acid is key for enhancing the reactivity. The reaction proceeds well under air, making the use of pure oxygen unnecessary. Each of the primary or secondary alcohols tested was oxidized to the corresponding aldehydes or ketones using this protocol.



Oxidation of alcohols to carbonyl compounds is among the most fundamental and important transformations in synthetic organic chemistry.[1] However, in typical oxidation reactions, a stoichiometric amount of harmful heavy metals is still used as oxidants, generating a large amount of chemical waste.[2] Therefore, significant attention has been paid to the development of catalytic reaction methods to replace classical oxidation procedures using stoichiometric quantities of inorganic oxidants, which are highly toxic and environmentally polluting. Increasing environmental concerns have led to the development of “green oxidants” such as molecular oxygen or hydrogen peroxide to minimize chemical wastes.[3] Although a large number of homogeneous and heterogeneous metal-catalyzed systems for the oxidation of alcohols with molecular oxygen have been developed, in most cases expensive or harmful transition metals such as Pd,[4] Pt,[5] and Au[6] have been used. Recently, a nitroxy radical (TEMPO)-catalyzed aerobic oxidation of alcohols has been reported;[7] however, much cheaper and greener systems are required, especially for industrial applications.[8,9]

We have focused on bismuth as an environmentally friendly catalyst for chemical reactions,[10] because it is generally cheap and relatively benign, and its salts behave as water-tolerant Lewis acids. Our laboratory has previously reported the reductive etherification of carbonyl compounds with alcohols,[11] asymmetric Strecker reactions,[12] allylation reactions,[12b] aldol reactions,[13] and Michael reactions[13] using bismuth salts as catalysts.[14] Examples of oxidation reactions using bismuth compounds have been reported by other groups; however, stoichiometric amounts of $Bi^{V}$ salts were used as an oxidant in these studies.[15]

Xu *et al.* reported the palladium-catalyzed aerobic oxidative esterification of benzyl alcohols.[16] In their report, the catalytic addition of a hydrosilane and bismuth chloride accelerated the reaction, and they hypothesized that the bismuth chloride promoted the formation of a hemiacetal or ß-hydride elimination of the intermediates. Chakraborty *et al.* reported $Bi_2O_3$-catalyzed alcohol oxidation; however, *tert*-butyl hydrogen peroxide (*t*-BuOOH) was used as an oxidant.[17] Recently, Lee *et al.* reported bismuth bromide-catalyzed alcohol oxidation with aqueous hydrogen peroxide.[18] Although oxidizing ability is expected, for bismuth, aerobic oxidation of alcohols using only a catalytic amount of bismuth salts has not yet been developed. Herein, we describe a new method of environmentally friendly air-oxidation reaction using a relatively benign, cheap bismuth salt as a catalyst.

First, we tested the aerobic oxidation of 1-phenyl-1-propanol **1a** in the presence of 20 mol% bismuth salt with 20 mol% nitric acid at 50 °C (Table 1). Of the 14 bismuth salts tested, we found that only $BiBr_3$ exhibited catalytic activity in the model reaction, affording the desired product in 69% conversion yield (entry 13), while the other bismuth salts displayed poor reactivity.

Next, we screened the reaction conditions focusing on oxygen and water (Table 2). Under air, the reaction proceeded to afford the oxidized product **2a** in 66% yield, *N*-(1-phenylpropyl)acetamide **3a** as a by-product in 12% yield, and the

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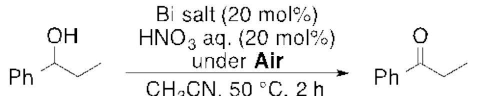
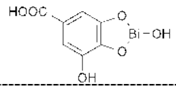
**Table 1.** Screening of bismuth salts as catalysts for the model reaction.




1a 2a

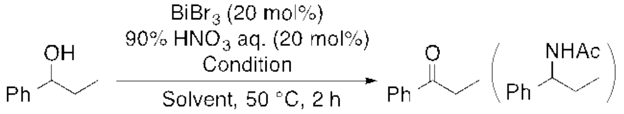
| Entry | Bismuth salt | Conversion yield[a] /% |
|---|---|---|
| 1 | $Bi(NO_3)_3$•$5H_2O$ | trace |
| 2 | $NaBiO_3$ | 2 |
| 3 | $Bi_2O_3$ | ND |
| 4 | Bi | 1 |
| 5 | $Bi(OH)_3$ | trace |
| 6 | BiOCl | trace |
| 7 | $Bi_2(SO_4)_3$ | ND |
| 8 | $Bi(OTf)_3$ | trace |
| 9 | $4Bi(NO_3)(OH)_2$•BiO(OH) | trace |
| 10 |  | trace |
| 11 | $BiF_3$ | 5 |
| 12 | $BiCl_3$ | 6 |
| 13 | $BiBr_3$ | 66 |
| 14 | $BiI_3$ | 2 |

[a] Conversion yield was determined by $^1$H-NMR analysis. ND: not detected.

recovered starting material **1a** in 15% yield (entry 1). Compound **3a** is a known product of the Ritter reaction, via nucleophilic attack by the nitrile solvent on the carbocation intermediate, which is derived from the reaction of alcohols with a Lewis acid or a Brønsted acid. Barrett *et al.* have reported bismuth-catalyzed Ritter reactions under slightly harsher conditions (100 °C, 17 h).[19] Accordingly, we conducted the reaction under oxygen (entry 2). Under an argon atmosphere, the reaction was sluggish and messy (entry 3). Considering both the convenience of the operation and the results of the reaction, we decided to investigate further optimization conditions under air. We subsequently investigated the effect of water on the reaction. Interestingly, under dry conditions (using MS4A), the reaction did not proceed even in air (entry 4). However, the addition of water suppresses the reaction (entries 5–7). Moreover, methanol was not suitable as a solvent in place of acetonitrile (entry 8). The other by-products in entries 1–3 were 2-bromo-1-phenylpropanone as an α-brominated product and etherified starting material. Henceforth, we investigated the aerobic oxidation reaction of **1a** at temperatures lower than 50 °C.

We investigated the effects of the acid at 30 °C (Table 3). Almost no reaction occurred using only nitric acid (entry 1). When we used $BiBr_3$ as a catalyst in the absence of acid, only the

**Table 2.** Effect of water, oxygen source, and solvents on the model reaction.

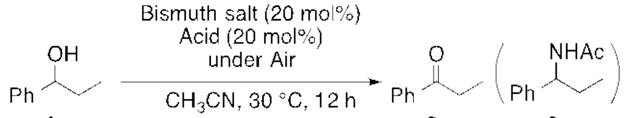



1a 2a 3a

| Entry | Condition | Solvent | Conversion yield[a] /% | | |
|---|---|---|---|---|---|
| | | | **1a** | **2a** | **3a** |
| 1 | under **Air** | $CH_3CN$ | 15 | 66 | 12 |
| 2 | under $\mathbf{O_2}$ | $CH_3CN$ | 11 | 73 | 8 |
| 3 | under **Ar** | $CH_3CN$ | 33 | 26 | 17 |
| 4[b] | under **Air** | $CH_3CN$ | 89 | 8 | 2 |
| 5 | under **Air** | $CH_3CN/H_2O$ = 9/1 | 61 | 33 | 5 |
| 6 | under **Air** | $CH_3CN/H_2O$ = 1/1 | >99 | - | - |
| 7 | under **Air** | $H_2O$ | >99 | - | - |
| 8 | under **Air** | $CH_3OH$ | >99 | - | - |

[a] Determined by $^1$H-NMR analysis. [b] In the presence of MS4A (100 mg/mmol).

**Table 3.** Effect of acid on a model reaction.




1a 2a 3a

| Entry | Bismuth salt | Acid | Conversion yield[a] /% | | |
|---|---|---|---|---|---|
| | | | **1a** | **2a** | **3a** |
| 1 | - | 90% $HNO_3$ aq. | 95 | - | 3 |
| 2 | $BiBr_3$ | - | 68 | - | 21 |
| 3 | $BiBr_3$ | 90% $HNO_3$ aq. | - | 79 (72)[b] | 10 |
| 4 | $BiBr_3$ | 35% HCl aq. | 59 | - | 32 |
| 5 | $BiBr_3$ | 96% $H_2SO_4$ aq. | 40 | - | 50 |
| 6 | $BiBr_3$ | 60% $HClO_4$ aq. | 45 | - | 44 |
| 7 | $BiBr_3$ | 98% HCOOH aq. | 60 | - | 22 |
| 8 | $BiBr_3$ | $CH_3COOH$ | 59 | - | 32 |
| 9 | $BiBr_3$ | $CF_3COOH$ | 71 | - | 20 |
| 10 | $BiBr_3$ | 85% $H_3PO_4$ aq. | 68 | - | 23 |
| 11 | $BiBr_3$ | 47% HBr aq. | 59 | - | 31 |
| 12 | $Bi(NO_3)_3$•$5H_2O$ | 47% HBr aq. | 88 | 9 | 2 |
| 13[c] | $BiBr_3$ | 90% $HNO_3$ aq. | 4 | 83 (82)[b] | trace |

[a] Determined by $^1$H-NMR analysis. [b] Isolated yield in parentheses. [c] 5 mol% $BiBr_3$ was used for 36 h.

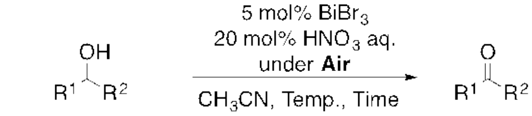
Ritter reaction occurred, affording by-product **3a** in 21% yield (entry 2). We found that the combination of a bismuth bromide with a suitable acid is key for the oxidation reaction (entry 3). The other acids were not as effective as nitric acid for this oxidation reaction (entries 4–11). Interestingly, the combination of bismuth nitrate with hydrobromic acid was not suitable for this oxidation (entry 12). Finally, when we prolonged the reaction time to 36 h, we succeeded in achieving a good isolated yield (82%) of predominantly **2a** using only 5 mol% $BiBr_3$ (entry 13).

Under the optimized condition, we screened the substrate scope on the aerobic oxidation reaction of secondary alcohols to corresponding ketones (Table 4). In an oxidation of simple benzylic alcohols cases, overreaction easily occurred to give the α-brominated compounds. However, oxidations of 1-indanol **1f** or 1-tetralol **1g** proceeded cleanly without over oxidation. On the contrary, the oxidations of aliphatic alcohols were relatively difficult to proceed compared to the benzylic alcohols **1i-1k** cases, therefore we conducted the oxidation reactions under oxygen.

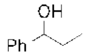
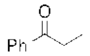
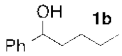
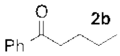
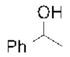
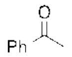
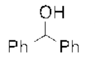
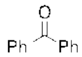
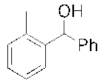
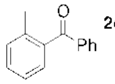
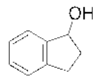
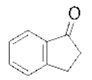
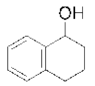
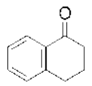
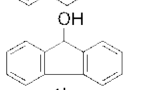
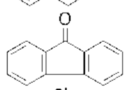
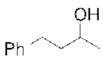
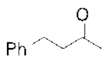
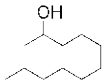
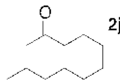
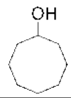
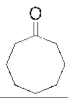
We also examined the aerobic oxidation of primary alcohols to aldehydes especially for the benzyl alcohol derivatives (Table 5). Benzaldehyde **6a** was isolated from benzyl alcohol **5a** in 90% yield after purification of column chromatography (entry 1). Tolaldehydes **6b, 6c** or naphtaldehydes **6d, 6e** were also obtained from corresponding alcohols **5b-5e** with high yields (entry 2-5). Several halogenated benzyl alcohols **5f-5j** were also oxidized in good to high yield except for 3-chlorobenzylalcohol **5g** (entry 6-10). We also tested the bulky substrate (entry 11), or electronic effect (entry 12, 13). This reaction was relatively suppressed by substrate having the electro donating group. Moreover, the oxidation of 3-phenylpropanol **5n** as an aliphatic alcohol was not observed in this reaction system (entry 14).

In summary, we developed aerobic oxidation of alcohols to the corresponding ketones or aldehydes by using a catalytic amount of $BiBr_3$, which is a cheap, relatively benign, and water-compatible Lewis acid as a catalyst. We found that the catalytic combination of $BiBr_3$ with nitric acid is key for enhancing the reactivity for the aerobic oxidation reaction. Further studies on the substrate generality of this reaction and on the reaction mechanism are currently in progress.

**Table 4.** Aerobic oxidation reaction of secondary alcohols to ketones.[a]

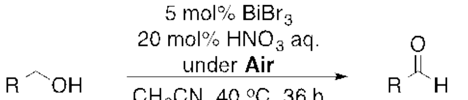



**1a-1k** (2.0 mmol) **2a-2k**

| Entry | Alcohol | Temp./°C | Time/h | Product (ketone) | Yield/% |
|---|---|---|---|---|---|
| 1 |  **1a** | 30 | 36 |  **2a** | 82 |
| 2 |  **1b** | 30 | 36 |  **2b** | 81(5)[b] |
| 3[c] |  **1c** | 30 | 36 |  **2c** | 56(14)[b] |
| 4 |  **1d** | 70 | 12 |  **2d** | 90 |
| 5 |  **1e** | 70 | 24 |  **2e** | 83 |
| 6 |  **1f** | 70 | 48 |  **2f** | 82 |
| 7 |  **1g** | 70 | 48 |  **2g** | 88 |
| 8 |  **1h** | 70 | 48 |  **2h** | 99 |
| 9[d] |  **1i** | 90 | 48 |  **2i** | 69 |
| 10[d] |  **1j** | 70 | 48 |  **2j** | 68 |
| 11[d] |  **1k** | 70 | 48 |  **2k** | 58(9)[b] |

[a] Isolated yield. [b] α-Bromo ketone of product (**4b, c** and **k**) was isolated, yield in parentheses. [c] 5.0 mmol scale. [d] Under $O_2$.

**Table 5.** Aerobic oxidation reaction of primary alcohols to aldehydes.[a]




**5a-5n** (2.0 mmol) **6a-6n**

| Entry | R | Yield/% | Entry | R | Yield/% |
|---|---|---|---|---|---|
| 1[b] | Ph | 90 (**6a**) | 8 | 4-$ClC_6H_4$ | 78 (**6h**) |
| 2 | 2-$MeC_6H_4$ | 88 (**6b**) | 9 | 4-$FC_6H_4$ | 77 (**6i**) |
| 3 | 4-$MeC_6H_4$ | 86 (**6c**) | 10 | 4-$BrC_6H_4$ | 93 (**6j**) |
| 4 | 1-naphtyl | 95 (**6d**) | 11 | 4-$^tBuC_6H_4$ | 86 (**6k**) |
| 5 | 2-naphtyl | 85 (**6e**) | 12 | 4-$NO_2C_6H_4$ | 92 (**6l**) |
| 6 | 2-$ClC_6H_4$ | 78 (**6f**) | 13 | 4-$MeOC_6H_4$ | 41 (**6m**) |
| 7 | 3-$ClC_6H_4$ | 37 (**6g**) | 14 | $Ph(CH_2)_2$- | trace (**6n**) |

[a] Isolated yield. [b] 5.0 mmol scale.

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## Supplementary Material

Supplementary data (general information, synthesis, procedure, and spectral data) associated with this article can be found, in the online version, at htpps://doi.org/10.1016/j.tetlet.xxxxxxxx.